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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 5

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SUBJECT: Review of PCB Source Methods in Recent Publications

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This memo presents the results of a literature review of methods used for PCB source identification or apportionment recently published in scientific journals (mid-1990s to present). No examples were located of studies that discriminated among different PCB sources based on differences in Aroclor composition. The majority of studies utilized congener-specific and/or homolog data (90 %). The few examples of Aroclor-based approaches were associated with limited objectives—when sources could be distinguished solely by spatial trends in total PCBs without considering composition, or to locate local sources of pollution by the patterns of a suite of contaminants, not PCBs alone. The authors of an exploratory study of apportioning sources through Aroclor-specific stable isotopic ratios (chlorine SIR) recommended that future studies of this method use congener-specific SIRs.

A broad search of the journals included in ScienceDirect® (www.sciencedirect.com) was performed for "PCB" and "source" (ScienceDirect® includes over 2000 titles). Two journals not included in ScienceDirect® were separately searched—Environmental Science and Technology (http://pubs.acs.org/journals/esthag/index.html) and Environmental Toxicology and Chemistry (www.setac.org). Titles generated by the search were initially screened by the abstracts. Acceptance depended on the media sampled (either solid media or biota/tissue, studies of water or air excluded), study objectives (involving techniques applicable to source identification or apportionment), and electronic availability of the complete paper (in practice, this excluded publications earlier than the mid-1990s).

Acceptance of studies did not depend on the study conclusions since the purpose of the review is to determine the methods used for PCB source identification or apportionment in papers accepted for publication in scientific journals. Therefore, inclusion of studies in the review does not imply USEPA endorsement of the conclusions of any particular study. This approach also ensures an unbiased sample of PCB source methodologies because the studies were not screened by outcome.

The search resulted in 30 applicable studies, approximately three-quarters for solid media (sediment, soil, or suspended particulates) and one-quarter for biota and human studies (Table 1). Most of the studies relied on congener-specific analyses or a combination of congener-specific and homolog analyses (87 %), one study used only homolog data (3 %), and three studies relied on Aroclor analyses (10 %).

There were no examples of distinguishing PCB sources on the basis of differences in Aroclor patterns. Of the three Aroclor studies in the review, one included total PCBs as a single input along with metals and other organic compounds in a multivariate analysis to identify local sources of pollution, but did not attempt to distinguish among different PCB sources (Scrimshaw and Lester 2001); one looked at spatial patterns of total PCBs to differentiate local sources from background (atmospheric deposition), but did not attempt to distinguish between sources by differences in Aroclor patterns (Stow, et al. 2005); and the authors of an exploratory attempt at source identification based on chlorine stable isotope ratios (SIR) in different Aroclors recommended that future studies be performed on a congener-specific basis (Reddy, et al. 2004). In summary, Aroclor data were only successfully used for source identification in specific circumstances—either when alternative PCB sources could be distinguished by spatial patterns of total PCBs, or when discrimination among alternate PCB sources was *not* a study objective.

The predominant approach for PCB source identification or apportionment is multivariate analysis of congener and/or homolog data—used in more than two-thirds of all studies in the review (three-quarters of the studies with congener data). The most common multivariate approaches are principle components analysis (PCA), factor analysis (FA), and polytopic vector analysis (PVA). Cluster analysis, classification trees, and discriminant analysis are less commonly used multivariate techniques for apportioning PCB sources. Other methods for comparing congener patterns include regression analysis, congener percent ratio[1], and graphic comparisons. Most studies also investigated spatial or temporal trends as an additional line of evidence of sources.

Another technique, neural (Kohenen) network, has been used for identifying sources of chlorinated dioxins and furans in sediments (Götz, et al. 1998), but an example involving PCB source identification was not located.

The pattern comparison approaches do not, of themselves, account for changes in congener patterns due to weathering, bioaccumulation, or trophic transfer, but the effects of such processes are sometimes modeled to improve the basis of the comparison.

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[1] Congener percent ratio (CPR) is a mathematical form of pattern comparison in which the congener fractions (percent contributions of individual congeners to total PCB) in environmental samples are divided by the respective congener fractions in comparison samples. Examples include comparison of PCB congener patterns in farmed fish and fish feed (Carlson and Hites 2005), and between sediment samples from separate locations potentially affected by different PCB sources (Kim, et al. 2000). The congener percent ratios would be 1 for all congeners if the congener patterns are identical in both sets of samples (and measured without error), and the variance of the congener percent ratios of all of the possible paired comparisons would be 0. The overall similarity between congener patterns was assessed by the variance of the congener percent ratios by Carlson and Hites (2005), and the similarity for any particular congener was assessed by T-tests of the respective congener fractions in the samples being compared by Kim et al. (2000). Note that the terms used in this approach have not been standardized. Carlson and Hite (2005) initially defined "percent congener ratio", but then used the term "congener percent ratio" in the text. Kim, et al. (2000) used the same ratio without a name. The term "congener fraction" is from Kim et al. (2000), but Carlson and Hite (2005) use the phrase "percent congener contribution".

An innovative approach is based on congener-specific stable isotopic ratio (SIR). Yanik, et al. (2003) investigated the use of congener-specific carbon SIR, which they referred to as compound specific carbon isotope analysis (CSIA), for identifying environmental transformations of PCBs and source apportionment of PCBs accumulated in biota. The results of this initial study "suggest that tracking PCB mixtures may be possible using CSIA techniques after standard chromatographic matching or other fingerprinting techniques become blurred". See Jarman, et al. (1998), Drenzer, et al. (2001), and Horii, et al. (2005) for more information. As mentioned earlier, a similar approach on an Aroclor-basis was less promising because of insufficient variability in SIR among Aroclors (Reddy, et al. 2004).

Analysis of enantiomeric fractions of chiral [2] PCB congeners in environmental samples is not included in Table 1 because, although the technique can reveal biometabolism of PCBs (Wong, et al. 2001; Robson and Harrad 2004), it does not appear to be applicable for distinguishing among weathered PCB sources. Robson and Harrad (2004) used chiral signatures to apportion atmospheric PCBs between two general sources: volatilization from soil and emission from PCB-containing products (transformers, capacitors, sealants). This approach was possible because the emissions from PCB-containing products are racemic [3], but soil PCBs are nonracemic due to enantioselective biodegradation in soil, which is reflected in the nonracemic PCBs that volatilize from soil. In other words, chiral signatures can be used to distinguish unweathered recent sources from biologically weathered older sources, but not when the PCBs of both sources have been biologically weathered.

Another approach not included in Table 1 is use of tracker pairs of congeners as evidence of weathering. The phrase "tracker pairs" refers to "congeners that maintain a constant relative proportion in sequentially more-highly chlorinated commercial Aroclors" (Karcher, et al. 2004), that is, pairs of congeners that exhibit the same ratio regardless of the source Aroclor. In this approach, changes in the ratio of congener tracker pairs in environmental samples from the "fixed ratio" in Aroclors are considered evidence that weathering has occurred (Karcher, et al. 2004). Since, by definition, tracker pair ratios are the same in any of the commercial Aroclors, they cannot be used to distinguish among different Aroclor sources.

[2] Nineteen of the 209 PCB congeners are chiral, which means they have alternative molecular structures that are mirror images (enantiomers). The chiral congeners of commercial Aroclors occur in equal proportions of both enantiomers, described as a racemic mixture. Biological processes that act on PCBs are often enantioselective (favoring one enantiomer over the other), so a finding of a nonracemic mixture (unequal proportions of enantiomers) in environmental samples or biota is evidence of biometabolism of PCBs (for example, by soil bacteria).

[3] The chemical and physical processes that affect atmospheric PCBs (for example, photolysis or atmospheric chemical reactions) are reportedly *not* entioselective (see reference in Robson and Harrad 2004), which means that racemic PCB emissions to the atmosphere are expected to remain racemic regardless of the amount of atmospheric modification.

Table 1. Summary of Recent PCB Source Identification Methods

Study	Medium	Analyte (number of congener groups)	Pattern Comparison	Trend	Multivariate Analysis						CMB	SIR
					CA	CT	DA	FA	PCA	PVA		
Ashley and Baker 99	sediment	congener (113) and homolog (separately)	homolog - graphic	spatial					x			
Bright et al 95	biota	congener (23)	graphic	spatial					x			
Cacela et al 02	sediment	congener (36)			x	x			x			
Carlson and Hites 05	biota	congener (115)	CPR						x			
Chiarenzelli et al 01	sediment	congener (10 most abundant), and 3 pesticides	graphic	spatial, radioisotope dating								
DeCaprio et al 05	human serum	congener (32)	graphic, statistical	receptor age						x		
Edgar et al 99	sediment	congener (22) and homolog (separately)	graphic	spatial					congener			
Hong et al 05	sediment	congener (22 for PCA, 111 for fingerprint)	graphic, statistical	spatial					x			
Huntley et al 97	sediment	coplanar congener (11)		spatial					x			
Ikenaka et al 05	sediment	coplanar congener (14)	graphic	temporal								
Ikonomou et al 02	biota	congener (138) and homolog (separately)	homolog - graphic					congener	congener		x	
Imamoglu and Christensen 02	sediment	congener (60)	statistical	spatial				x			x	
Imamoglu et al 04	sediment	congener (24)	statistical					x				
Johnson et al 00	suspended particles	congener (27)	graphic							x		
Kannan et al 97	sediment	homolog	graphic, table	spatial								
Kim et al 00	sediment	congener (71)	CPR, statistical	spatial								
Li et al 05	sediment	congener (28)	statistical	temporal				x				
Löffler et al 00	human blood	congener (4) and other organics (together)		spatial					x			
Magar et al 05	sediment	congener (54)	graphic	spatial						x		
Ogura et al 05	sediment	coplanar congener (14)	graphic	temporal				x			MC	
Rachdawong et al 98	sediment	congener (8)							x		x	
Reddy, et al 00	sediment	Aroclor										chlorine
Ross et al 04	biota	congener (109), PCDD, and PCDF (together)	graphic	spatial					x			
Samara et al 05	sediment	congener (14)		spatial								
Scrimshaw and Lester 01	sediment	Aroclor (1), metals, and other organics					x		x			
Stow et al 05	soil	Aroclor (1)		spatial								
Watanabe et al 05	biota	coplanar congener (12), PCDD, and PCDF	graphic						x			

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					CA	CT	DA	FA	PCA	PVA		
		(together)										
Yanik et al 03	biota	congener (22)										carbon
Yao et al 02	sediment	coplanar congener (14)	statistical	temporal								
Zhang and Jiang 05	sediment	indicator congeners (6)		spatial					x			

Notes to Table 1:
CA – cluster analysis
CMB – chemical mass balance
CPR – congener percent ratio
CT – classification tree
DA – discriminant analysis
FA – factor analysis
MC – monte carlo
PCA – principle components analysis
PVA – polytopic vector analysis
SIR – stable isotopic ratio
statistical – statistical methods of pattern comparison (e.g., multiple regression) other than the techniques listed under multivariate analysis
table – homolog patterns are compared by data presented in parallel rows

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